

# SEPARATION AND CONCENTRATION OF VOLATILE ORGANIC CONTAMINANTS BY ACTIVATED CARBON CLOTH FOR CRYOGENIC RECOVERY

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## Introduction

New air quality control regulations and economics are causing the development of new devices or the optimization of existing technologies for control of toxic emissions from industrial sources. Toxic chemicals are emitted into the atmosphere from facilities within the United States at a rate of  $1.1 \times 10^6$  kg/year [1]. Volatile organic contaminants (VOCs) account for 47%, and non-halogenated VOCs account for 36% of these toxic emissions [1]. For these emissions, under the 1990 Clean Air Act Amendments (CAAA), the United States Environmental Protection Agency (USEPA) should establish maximum achievable control technology (MACT) standards. MACT standards are based on best control technologies that offer the maximum degree of emission control [2]. MACT will have important effects on specific VOC sources within the next eight years because all MACT standards are required to be promulgated by 15 November 2000, and a source subjected to MACT standards must achieve compliance within three years of promulgation of the standards. Sources that must comply with the new VOC standards are related to food processing, wastewater treatment, electronic manufacturing, petroleum refining, petrochemical manufacturing, asphalt production, pharmaceutical industry, polymer and resin manufacturing, solvent production, and dry cleaning industry.

Based on an economic and engineering study about VOC control technologies [3], if the VOCs have a value > \$0.66/kg then carbon adsorption and vapor recovery should be considered. Dyer and Mulholland [3] indicated that carbon adsorption is the most cost effective technology for gas flow rates > 1,000 scfm and VOC concentrations > 500 ppmv. Moreover, variable flow rates and variable VOC concentrations are not disruptive for carbon adsorber performance [4], and they do not produce secondary pollutants. But, conventional carbon adsorbers can achieve recovery efficiencies up to 98% which may not be sufficient for MACT standards.

New carbon adsorption recovery systems can be developed that achieve higher recovery efficiencies while providing better economical and technical advantages over existing ones. For this purpose, we have developed a new activated carbon cloth (ACC) adsorption system that has been integrated with electrothermal desorption and cryogenic condensation to reduce the amounts of VOC emissions to MACT standards and provide for reuse of the VOCs that are recovered.

In this system liquid nitrogen (LN2) is used as the required refrigerant. LN2 can reduce VOC emission concentrations to ppbv levels due to its high cooling capacity and low temperature. One advantage of the LN2 system compared to other refrigeration systems is the multiple use of LN2. First, the cooling capacity of LN2 is used to condense VOCs. Then, the evaporated  $N_2$  can be used for other process needs such as inerting and safety blanketing. Another advantage of LN2 refrigeration over conventional mechanical condensation systems is the absence of moving parts such as compressors. But, LN2 consumption rate is high for typical industrial effluent concentrations. The effluent VOC concentrations are typically <1% by volume due to the limitations caused by their lower explosion limits. Ideal LN2 consumption (minimum mass of LN2 required per unit mass of VOC recovered in an isolated thermodynamical system) is linearly related to the inverse of the VOC concentration (Figure 1). If the VOC concentration can be increased, then LN2 consumption can be decreased. This is due to the fact that some portion of the cooling capacity transfers to the noncondensable carrier gas. Therefore, ACC adsorption technology is used to pre-concentrate the effluent VOCs for an efficient vapor recovery.

In the developed system, ACC adsorption is followed by electrothermal regeneration resulting in formation of a concentrated organic vapor which is cryogenically condensed from the gas phase. Electrothermal desorption allows for optimizing the desorption time and the concentration profile of the desorbed VOC to allow minimal use of cryogen. This system can enable VOC sources to meet air quality control regulations while providing a high quality liquid VOC product for reuse.

## Description of the laboratory scale system

The laboratory scale ACC adsorption-cryogenic vapor recovery system is presented in Figure 2. Sample gas is generated by passing ultra-high purity (UHP)  $N_2$  gas through VOC liquid and saturating the gas stream. The saturated stream is then mixed with the second pure  $N_2$  stream to produce a gas sample with desired VOC concentration and total flow rate. The sample gas generation system is calibrated using a gas chromatograph/mass spectrometer (GC/MS, Hewlett Packard GC 5890 and MS 5971), a gas chromatograph/flame ionization detector (GC/FID, Hewlett Packard GC 5830A), UHP  $N_2$  gas and a Matheson calibrated VOC gas mixture. The calibrated gas stream passes through the fixed bed of ACC, where the organic material is separated from the carrier gas by adsorption. After breakthrough of VOC from the fixed bed, pure  $N_2$  gas is passed through the adsorption bed and electrical power is supplied to the ACC. Electrical energy regenerates the adsorption capacity of the ACC and provides a  $N_2$  gas stream containing desorbed VOC. VOC concentration in the  $N_2$  carrier gas is controlled by the supplied electrical power and the flow rate of the carrier gas. The concentrated vapor stream is then directed to a custom shell-and-tube cryogenic condenser where the VOC is condensed on the condenser's internal cold surfaces. The condensed VOC is transferred from the bottom of the condenser into an Erlenmeyer flask.

## Activated Carbon Cloth Adsorbent

ACC, which is made of woven activated carbon fibers (ACFs), is an efficient adsorbent to separate VOCs from gas streams. Compared with activated carbon pellets (ACPs), granular activated carbons (GACs) or powder activated carbons (PACs), ACCs have a higher contact efficiency, higher specific surface area for a higher specific pore volume, 10 to 100 times faster adsorption and desorption rates [5]. These properties are mainly due to the existence of no macropores, no or little mesopore volume, and more uniform distribution of micropores from the external surface to the core of fiber [6]. ACC's rapid adsorption and desorption rates can reduce the required process cycle time and increase the bed adsorption capacity by reducing the length of mass transfer zone (MTZ). Due to its cloth form, ACC can be installed in different configurational forms inside fixed beds providing different adsorption and desorption performance as well as specific pressure drop (Pa/gm adsorption). Suitability for in-situ electrothermal regeneration and easy handling are other advantages of ACC.

ACC samples were obtained from American Kynol, a subsidiary of Nippon Kynol, located in Pleasantville, NY. Kynol's ACCs are made of novoloid fibers (polymerized cross-linked phenolic-aldehyde fibers). Novoloid fibers have an amorphous network structure containing 76% carbon, 18% oxygen, and 6% hydrogen [9]. These fibers are woven by conventional textile techniques to produce a novoloid cloth. The cloth is then carbonized and activated in an O<sub>2</sub> free atmosphere using steam or CO<sub>2</sub> at 900 °C in a one step process to produce ACC. Carbon content of ACC is typically 95% with oxygen and hydrogen contents of 4% and 0.7%, respectively [10]. Pore volume and pore size of the ACC increase with increasing duration of activation. The resulting micropores are slit shaped and remain uniform from the external surface to the core of the fiber [6].

Kynol™ ACC-5092-20 was identified as a suitable ACC adsorbent for the VOC concentration range of industrial emissions (in the order of 1% by volume). ACC-5092-20 have a higher adsorption capacity than the other Kynol's ACCs for 1% by volume concentration of the VOCs considered for the system evaluation tests (acetone, methyl ethyl ketone and toluene). This is mainly due to the existence of a high specific pore volume and high volume ratio for pore widths in the supermicro, transitional range, and mesopores close to the transitional range. SEM micrographs of the ACC sample are provided in Figure 3. Mesopores and transitional micropores can be seen from the SEM micrograph of the ACC's fiber cross section. The cumulative pore size distribution of the ACC sample in comparison with some other adsorbents is given in Figure 4. Specific surface area and micropore volume of ACC-5092-20 were measured with a Micromeritics ASAP 2400 using nitrogen at liquid nitrogen temperature. The BET specific surface area of the sample was 1592 m<sup>2</sup>/g. The specific micropore volume was 0.69 cm<sup>3</sup>/g.

## Fixed Bed of Activated Carbon Cloth

In the fixed bed ACC layers are installed in parallel to each other in a cross flow fashion. This allows for flexibility in effective adsorption bed length and apparent ACC density. With a 1.14 mm separation distance between each layer, an apparent ACC bed density of 94.5 mg/cm<sup>3</sup> results. The bed packing density can be increased to 800 mg/cm<sup>3</sup> (0.47 total porosity). In the fixed bed, the ACC layers are connected electrically in parallel in three separate modules. The modules are connected electrically in series. The resulting circuit is connected to electrodes of a 120 V a.c. source controlled by a Variac. This arrangement is expected to result in uniform electrical heating and carefully controlled VOC desorption.

## Electrothermal Regeneration of Activated Carbon Cloth

In electrothermal regeneration process an electric current is passed through the fibers. Electrical work due to phonon and defect scattering [11] in ACC is directly transformed to thermal energy in the ACC and the adsorbed VOC. By the continuous flow of electric current, the thermal energy of the adsorbed molecules increase to a level that overcome the surface bonding energy, and the VOC desorbs from the ACC. Since electrical work is transformed to desorption energy directly, the carrier gas temperature can be substantially lower than the ACC temperature. The temperature gradient along the bed is positive, and along the fiber radius is negative (or zero, depending on the value of fiber Biot number). In conventional thermal desorption methods, the temperature gradient along the bed is negative and along the fiber radius is positive. These effects cause positive desorption rate contributions for electrothermal desorption due to the heat transfer, Soret effect and pore effusion. While, mass transfer contributions are negative for conventional thermal desorption methods. Therefore, electrothermal regeneration should have higher energy efficiency compared to conventional thermal regeneration methods. Another advantage of electrothermal desorption is that the energy transfer rate can be very high and controlled easily. This enables careful control of desorption time and effluent VOC concentration profile for a better cryogenic recovery.

## Results and Discussion

The laboratory-scale fixed bed configuration was used to measure breakthrough curves. For each breakthrough test, total gas flow rate through the bed was 5 slpm. VOC concentration of the inlet gas stream was measured before passing through the fixed bed. Gas phase VOC in the bed was sampled from the sampling ports along the bed's length and analyzed intermittently using the GC/MS and continuously using GC/FID (Figure 2). Sample results for MTZ distribution curves describing how acetone concentration changed with time and location within the bed are presented in Figures 5. Breakthrough time was 75 min when using three ACC modules containing 27.05 g ACC and a packing density of 94.5 mg/cm<sup>3</sup>. Breakthrough was followed by a saturation time of 58.5 min. Saturation time is defined as the time required for the effluent concentration (C<sub>out</sub>) to increase from 5% to 95% its inlet concentration (C<sub>in</sub>).

The breakthrough curve for the bed outlet exhibit a standard diffusion mass transfer limited behavior in the form of:  $C_{out} = C_{in} (1 + \exp[(K' - t)/\tau])^{-1}$  where  $\tau$  is the stoichiometric time (time for C<sub>out</sub>=1/2 C<sub>in</sub> or  $\tau = W_s/C_m F$ , where W<sub>s</sub> is bed VOC adsorption capacity at C<sub>in</sub> and F is the total gas flow rate), and K is a constant that depends on the effective diffusion resistance of the MTZ. From these results, dynamic adsorption capacity of the ACC for 1% by volume acetone is 456 mg/g or 0.581 cm<sup>3</sup>/g. Equilibrium isotherm for adsorption and

desorption of acetone and ACC-5092-20 can be classified as BDDT type IV isotherm. Due to capillary condensation in mesopores, the isotherm has a hysteresis region at high concentration values. The equilibrium micropore adsorption and capillary condensation capacities of the ACC for 1% by volume acetone were measured to be 401 mg/g and 93.6 mg/g, respectively.

Effect of packing density on adsorption dynamic is presented in Figure 6. A smaller packing density results a shorter breakthrough time and a larger MTZ due to axial dispersion and mixing effects. Increasing packing density from 94.5 mg/cm<sup>3</sup> to 450 mg/cm<sup>3</sup> increases the breakthrough time from 75 min to 91.7 min. Since a higher packing density produces a larger pressure drop, it is possible to find an optimum set of packing density and pressure drop for a minimum cost.

Regeneration tests for a saturated fixed bed of ACC were performed to evaluate the effect of applied electrical power (Figure 7). N<sub>2</sub> gas flow rate through the bed was controlled at 1 slpm for three tests and 0.5 slpm for two tests. Electrical voltage for each test was set at select values to observe the effect of applied electrical power profile on the resulting effluent VOC concentration and bed temperature profiles. Effluent maximum VOC concentrations during desorption range from 18% to 63% by volume. VOC concentration profile and desorption time is readily controlled by carrier gas flow rate and applied electrical power. Increasing VOC concentration was observed with decreasing carrier gas flow rate and increasing applied power. In all five tests, more than 75% of the adsorbed acetone was regenerated at a bulk gas temperature of < 80 °C and an effluent concentration of > 10% by volume. Low resulted bulk gas temperature is indicative of an efficient energy transfer. Effect of generated high effluent concentration values on improvement of LN<sub>2</sub> consumption and amount of vapor recovery can be examined from Figure 1. Moreover, the high effluent concentrations enable the cryogenic condenser to operate at warmer temperatures while achieving high recovery efficiencies.

Cryogenic vapor recovery efforts are discussed in the next paper [12].

## Conclusions

A novel activated carbon cloth (ACC) adsorption/electrothermal regeneration/cryogenic system was developed to separate, concentrate and recover volatile organic contaminants from industrial gas streams. ACC demonstrates good performance characteristics due to its high contact efficiency, high adsorption capacity, and ease in handling. Electrothermal regeneration provided fast desorption rates and efficient energy transfer. Electrothermal regeneration concentrated VOC vapors up to 63% by volume without optimization. Concentrating the gas stream, drastically reduces the amount of cryogen required to condense the VOC from the gas stream end enables the condenser to operate at warmer temperatures while achieving a high recovery efficiency.

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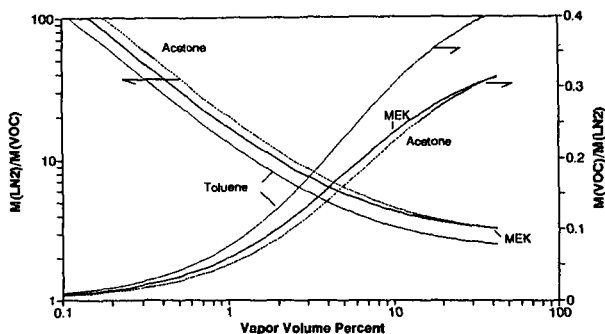


Figure 1. Ideal mass of LN2 required per unit mass of VOC recovered and ideal mass of VOC that can be recovered per unit mass of LN2.

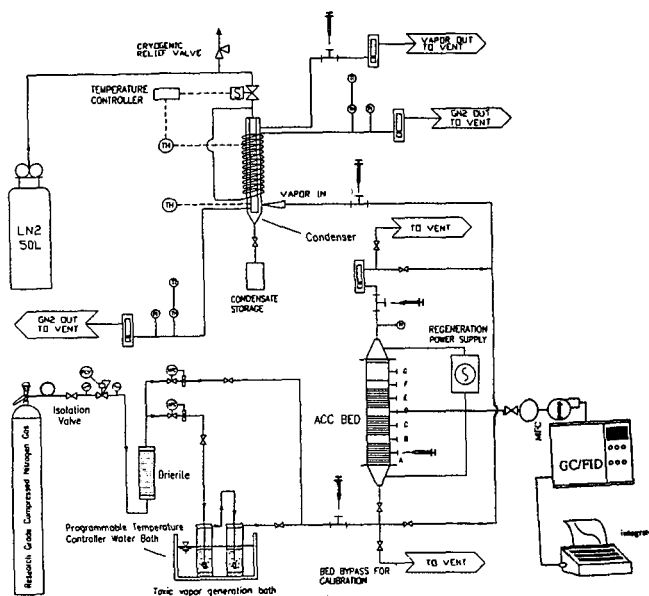


Figure 2. Integrated adsorption/electrothermal regeneration/cryogenic vapor recovery system.

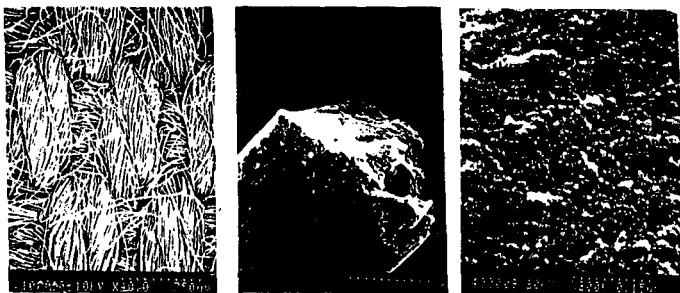


Figure 3. SEM micrograph of ACC-5092-20 and fiber cross section.

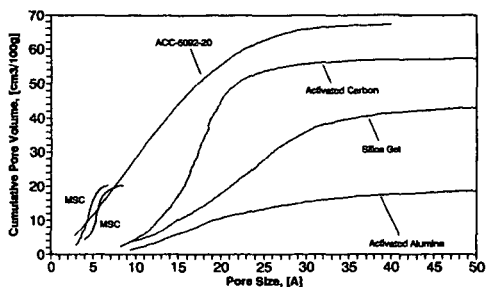


Figure 4. Cumulative pore-size distribution for ACC-5092-20 [7] compared with some other adsorbents [8]

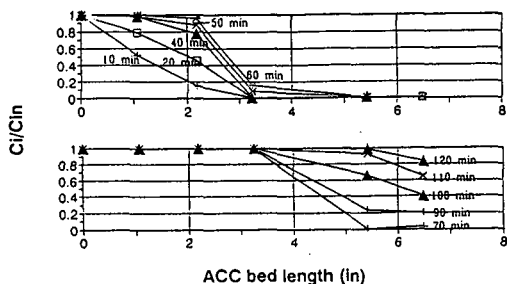


Figure 5. Mass transfer zone movement through the ACC bed. Inlet concentration: 1% acetone in N<sub>2</sub>. Total gas flow rate: 5 slpm.

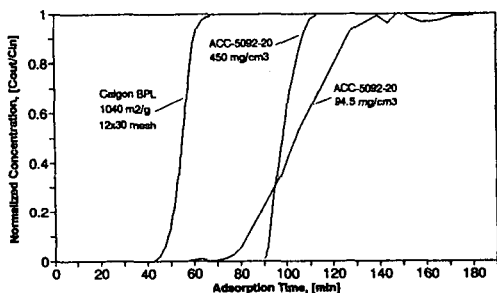


Figure 6. Effect of packing density on the dynamic characteristics of breakthrough.

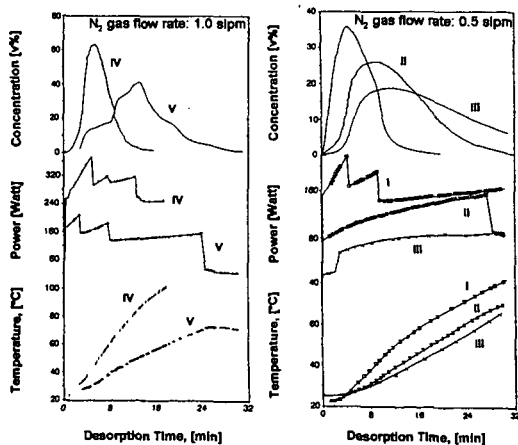


Figure 7. Electrothermal regeneration test results.